BYU

PREDICTING MICROSTRUCTURE AND PERFORMANCE FOR OPTIMAL CELL FABRICATION

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Project ID # ES220

OVERVIEW

Timeline

- Project start date: Apr 2013
- Project end date: Mar 2017
- Percent complete: 50%

Budget

- Total project funding: $794,000
  - (DOE share 100%)
- Funding received in FY14: $198,500 (12 months)
- Funding for FY15: $198,500 (12 months)

Barriers

- Cell performance
  - 200 Wh/kg (EV requirement)
- Life
  - 3000 cycles (PHEV 40 mile requirement)
  - Calendar life: 15 years.
- Cost

Partners

- Industrial collaboration with A123, Hydro-Québec
- Research collaborations with LBNL, ANL, and others

RELEVANCE

- Program Objectives:
  - Develop rapid and reliable tools for measuring and predicting electronic and ionic conductivities and 3D microstructures of particle-based electrodes
  - Understand tradeoffs and relationships between fabrication parameters and cell performance

- Current-Year Objectives:
  - Simulate electrode fabrication process to predict electrode morphology (Toda 523) using dynamic particle packing model
  - Fabricate first-generation ionic conductivity and N-line electronic conductivity probes

- Impact on DOE Barriers for EVs/PHEVs:
  - This work addresses a longstanding unmet industry need to be able to conveniently quantify electronic and ionic conductivities of thin-film electrodes and current collector contact resistance—solving this problem will accelerate process improvement.
  - This work remedies our poor understanding of the influence of fabrication parameters on heterogeneities in microstructure, which affect cell energy, power, and cycle life.

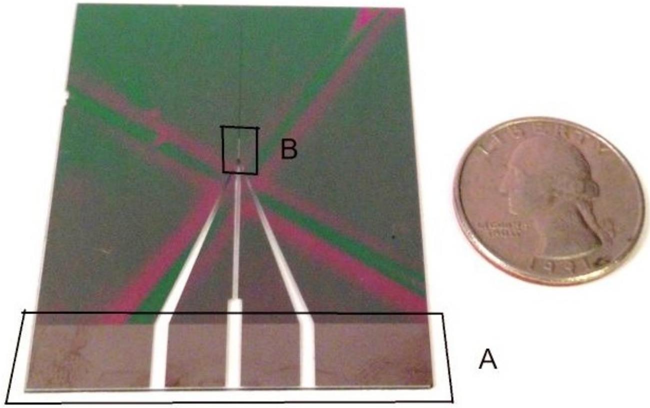
MILESTONES

- **June 2014**: Determine appropriate set of descriptors or metrics that effectively characterize previously observed microstructures. *Complete*
- **Sept 2014**: (Go/No-Go) Discontinue current 4-line probe geometry if measurement variability is not significantly less than sample-to-sample variability. *Decision: Go*
- **Dec 2014**: Develop local ionic conductivity probe and demonstrate method by testing two candidate electrode materials. *Complete*
- **Mar 2015**: Use dynamic particle-packing (DPP) model to predict electrode morphology of Toda 523 material. *Complete*
- **June 2015**: Develop fabrication process of micro-N-line probe and demonstrate method by testing two candidate electrode materials. *On track*
- **Sept 2015**: (Go/No-Go) Discontinue dynamic particle-packing (DPP) model if predictions are not suitable match to real electrode materials. *On track*

APPROACH

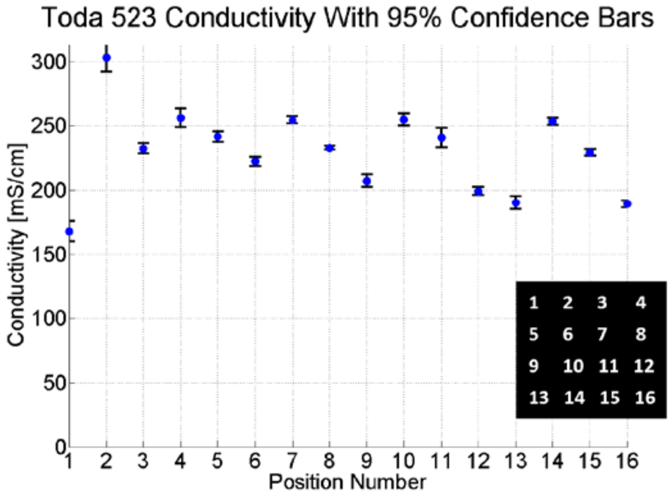
- Construct novel micro-N-line surface probes that can sample local conductivity of intact battery electrodes. The method overcomes multiple problems with previous methods, allowing reliable measurements of:
  - Bulk film conductivity while electrode still attached to metallic current collector
  - Contact resistance to current collector
  - Effects of pressure and presence of electrolyte
  - Spatial variations and anisotropy
- Construct a particle-dynamics model that can predict electrode microstructure and conductive pathways. The model will uniquely:
  - Predict effects of fabrication variables (slurry composition, drying, calendering, etc.)
  - Be validated with extensive experiments

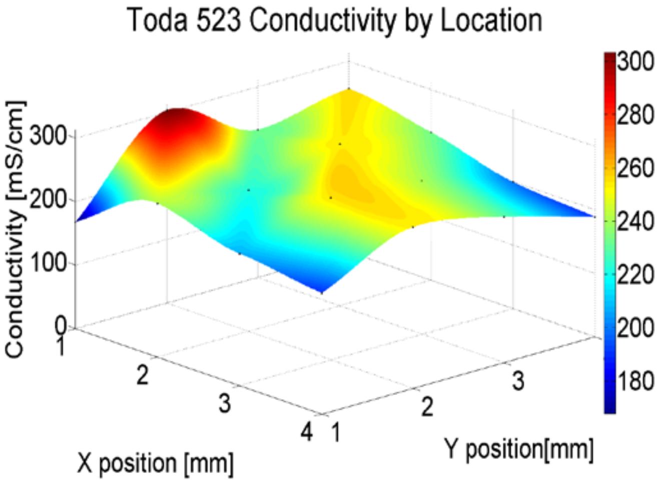
PREVIOUS TECHNICAL ACCOMPLISHMENT (FY 2013): FOUR-LINE-PROBE FABRICATION AND MEASUREMENT



Completed micro-four-line-probe showing: (A) exposed connection pads, and (B) window for exposing the four contact lines.

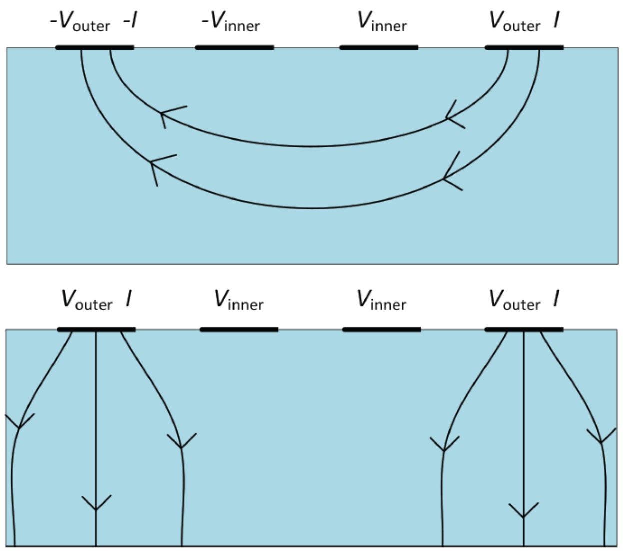
- Micro-four-line-probe was fabricated in the BYU Cleanroom with conducting lines 10 microns apart.
- Because the spacing of the contacts is on the order of the cathode material thickness, the probe current probes the cathode material conductivity properties *without* large amounts of shunt current passing through the current collector metal film.

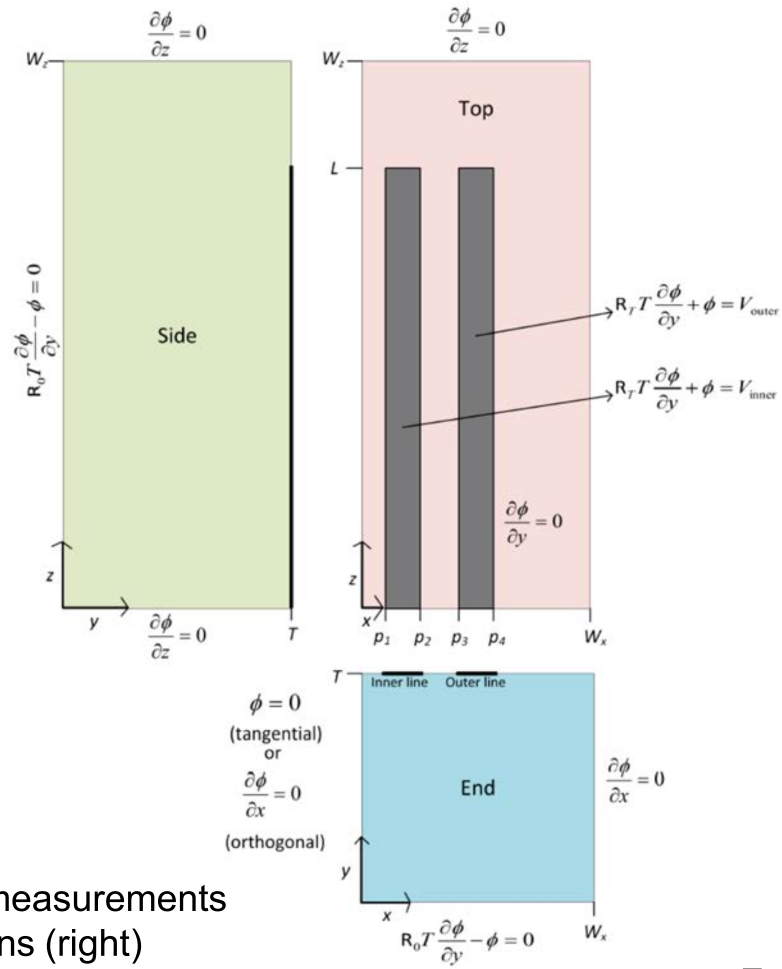




Technical Accomplishment (Oct 2014): Improved Inversion Procedure

- To get both conductivity and contact resistance from one set of micro-four-line-probe measurements previously required expensive finite-element computations.
- A hybrid **analytical-numerical** inversion procedure was developed. This advance allows for **accurate real-time inversion of measurement data** using an in-house optimization routine.

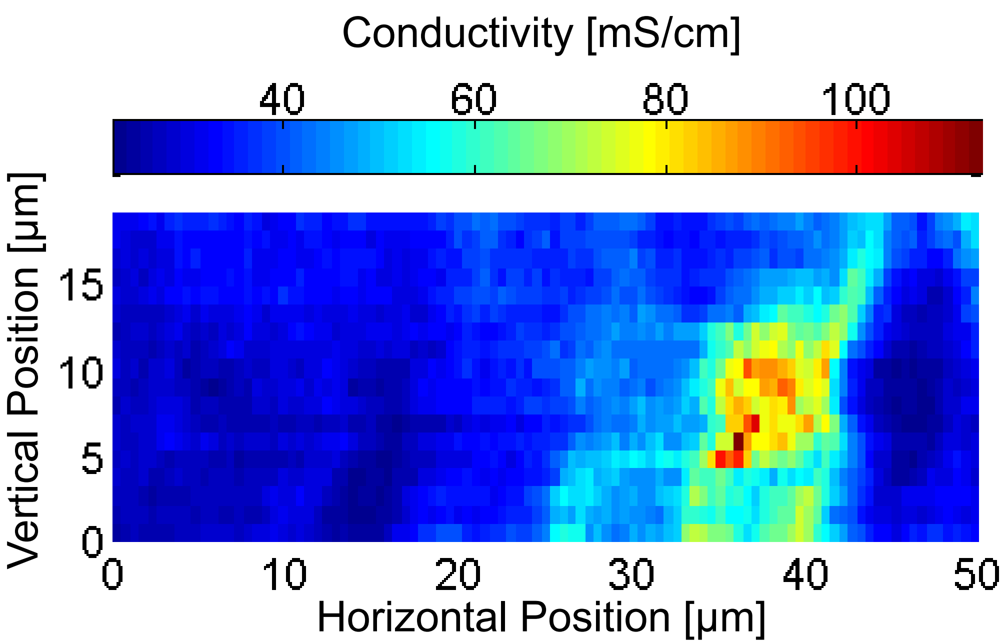


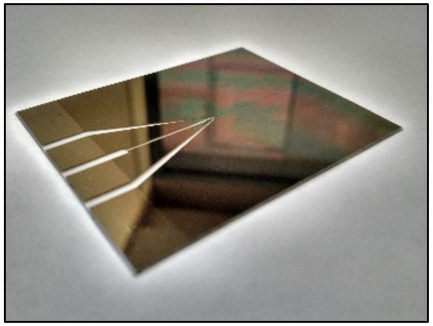


Tangential (top) and orthogonal (bottom) electrical measurements are interpreted under realistic 3D boundary conditions (right)

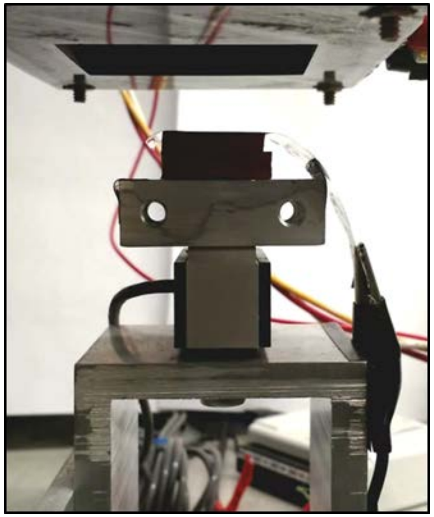
Technical Accomplishment (Dec 2014): High-Res Mapping of Conductivity Variability

1900-point map of commercial-quality Toda NCM 523 electrode shows significant heterogeneity in conductivity.





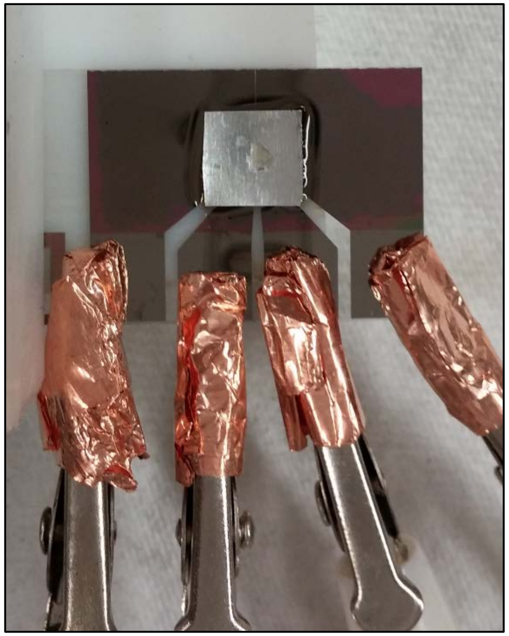
Probe (top) and mounting apparatus (below)



Technical Accomplishment (Mar 2015): Preliminary Ionic conductivity measurements

Four-line-probe concept adapted to measuring local ionic conductivity of electrode films:

- 6 electrode films, 2 separators, and 5 probe designs were tested.
- Initial proof-of-concept experiments were completed, but showed large uncertainties ($\pm$40% from expected conductivity results).
- Additional work is needed to overcome the materials challenges in the ionic environment to obtain a robust probe design and method.

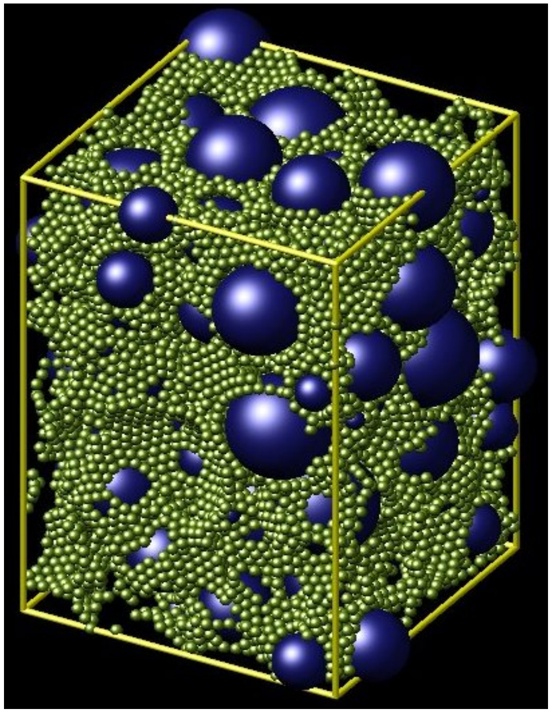


Relative Ionic Conductivity

Film	$k_{\mathrm{eff}}/k_{\mathrm{int}}$
ANL HE5050 cathode	0.12
ANL graphite anode	0.08

Micro-four-line-probe with electrode film sample on top. Sampling area for ionic conductivity is 70 x 500 µm.

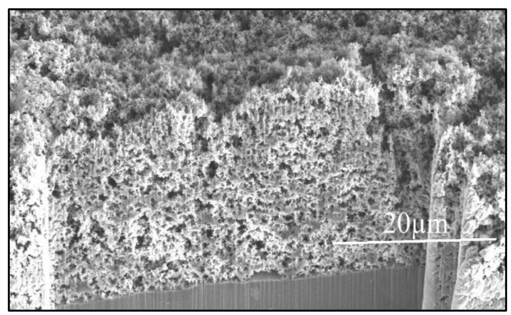
Technical Accomplishment (Mar 2015): Dynamic Particle Packing Model



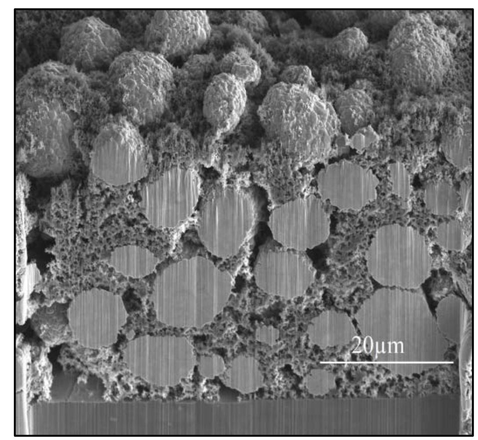
The particle model is designed to predict slurry viscous behavior, microstructure changes during drying and calendering, and solid mechanical and conductive behavior.

A particle-based model (left) uses superpositions of spheres to represent active material (blue) and carbon/binder/solvent domains (green). The only inputs to the model are interaction force curves between the spheres.

The model was developed and experimentally validated in two parts:

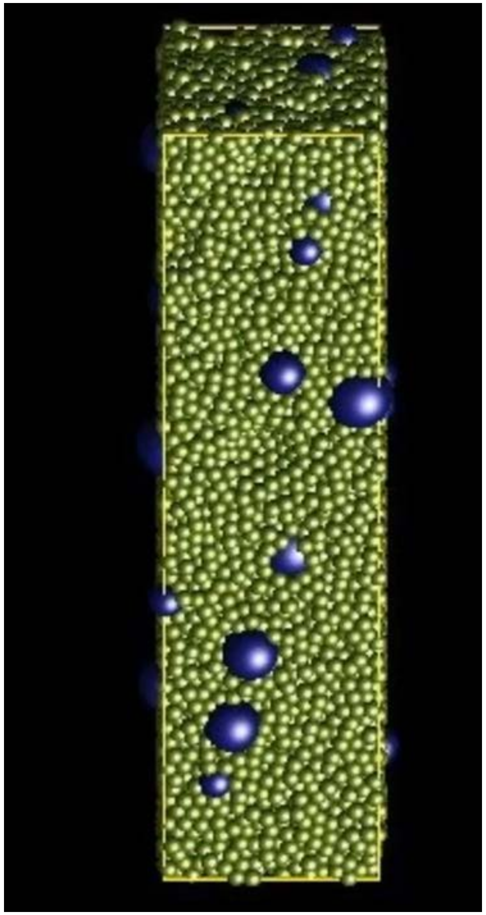


(1) Simulate slurry and dried film made from carbon black and binder

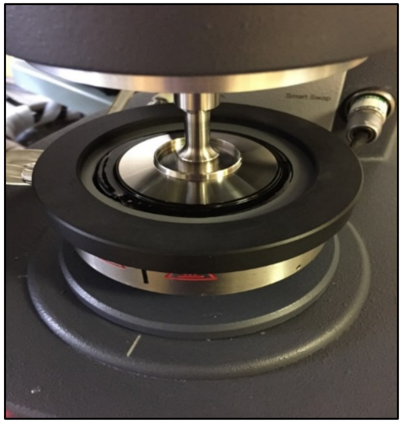


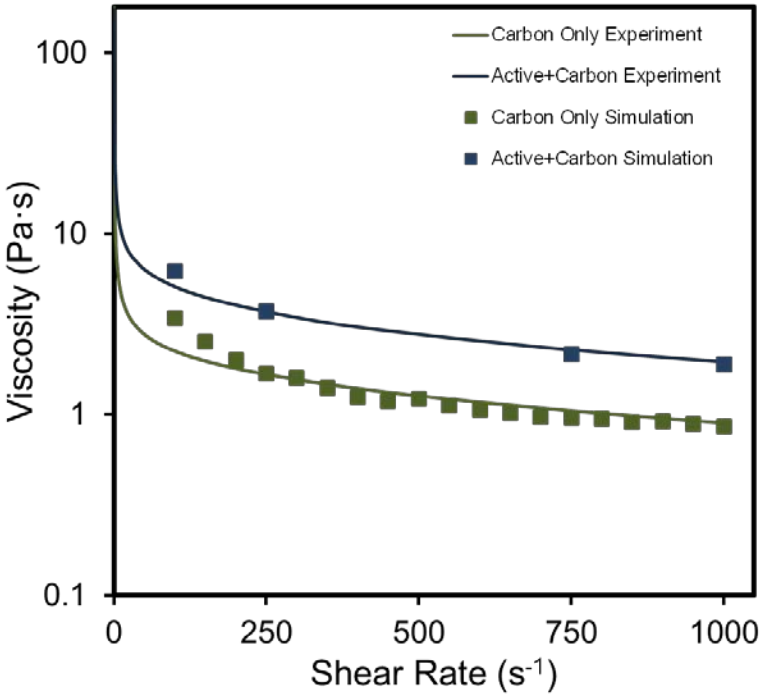
(2) Simulate slurry and dried film additionally containing Toda 523 active material

Technical Accomplishment (Mar 2015): Simulate Viscosity of Electrode Slurry



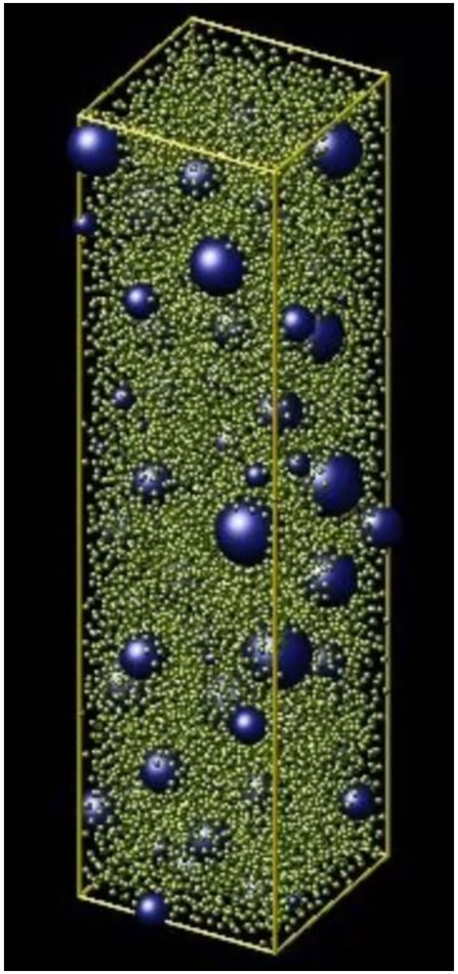
Simulation (left) and experimental apparatus (right) used to determine slurry viscosity as a function of shear rate, over the range relevant to commercial battery fabrication





Simulations predict the viscosity changes relevant to slurry mixing and film formation

Technical Accomplishment (Mar 2015): Simulate Properties of Dried Electrodes

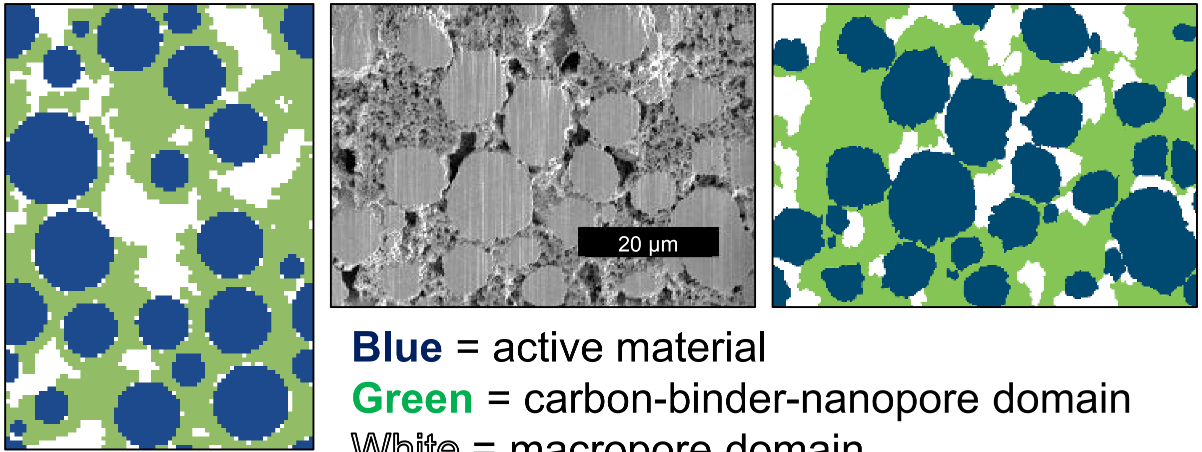


During drying the carbon particles (green) become more attractive to each other and to the active material (blue)

Shrinkage Ratio

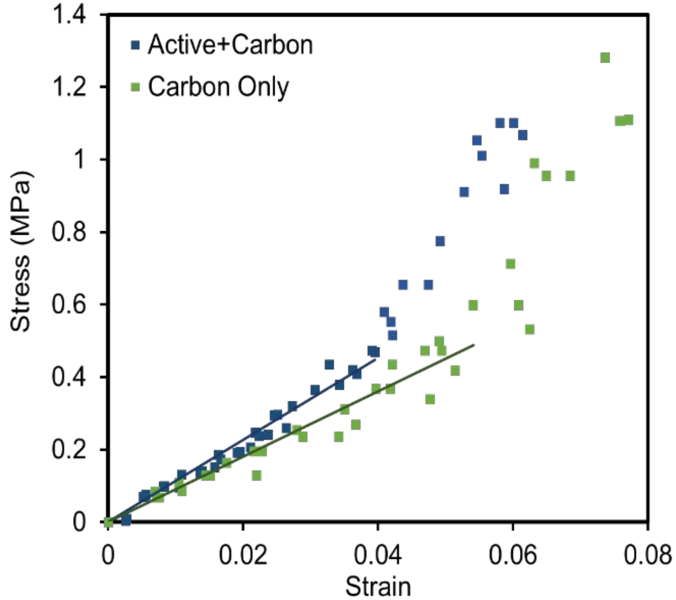
Film	Exp	Sim
Carbon	8.6	8.2
Active+C	3.3	2.6

Simulated cross section (left) compared to experimental results. The SEM/FIB image (center) is segmented (right) using computer tools developed at BYU.



Blue = active material
Green = carbon-binder-nanopore domain
White = macropore domain

Technical Accomplishment (Mar 2015): Simulate Properties of Dried Electrodes



Experimental testing of elastic modulus of multiple films

Elastic modulus (MPa)

Film	Exp	Sim
Carbon	9.0	9.3
Active+C	11.3	11.6

The model predicts substantial anisotropy in electronic and ionic conductivity of active film prior to calendering.

Direction	Relative Cond
In-plane	1.16
Out-of-plane	0.69

Simulation also exhibits

- Negative in-plane stress of dried film
- Permanent deformation of film upon calendering

Responses to Previous Year Reviewers' Comments

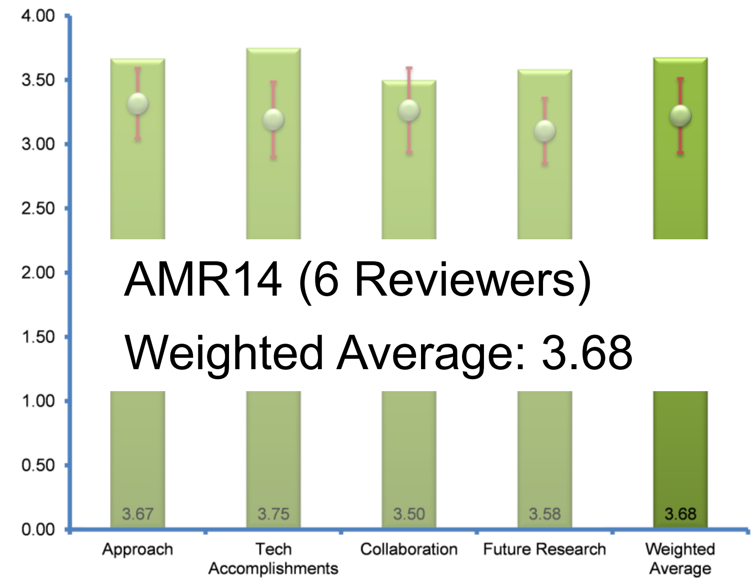
This project was favorably reviewed during AMR14 with generally positive comments. Three main concerns:

1. Control errors in measurements:

   Along with the improved inversion routine, a statistical procedure to accept/reject data was recently implemented for greater accuracy in electronic conductivity. Different probe geometries were tested in FY2014 to find optimal design for reliability.

2. More challenging aspects of the project in later years:

   Development and validation of the dynamic particle model and completing ionic conductivity measurements are indeed difficult. Challenges are being addressed as they arise.



3. Collaboration:

   More materials can now be measured as our process has improved, and we have received materials for testing from Hydro-Québec, A123, and ANL. Transfer of technology to A123 is well advanced. We are seeking additional collaborations.

COLLABORATIONS AND COORDINATION

- **A123** non-contract partnership
  - This project was initiated at A123's request for technology they needed but lacked.
  - A123 and BYU provide materials and expertise to each other.
  - A123 purchased BYU's conductivity probe technology to enable process improvement for their electrode fabrication process. Two probes and associated computer program have been delivered by BYU.
- Non-contract **research collaborations** within the battery research community, involving exchange of battery materials and expertise:
  - Andy Jansen, ANL
  - Vince Battaglia, Venkat Srinivasan, and Gao Liu, LBNL
  - Karim Zaghib, Hydro-Québec
  - Claire Grey, Univ. of Cambridge
  - Simon Theile, Univ. of Freiburg / IMTEK

Remaining Challenges and Barriers

- Extend successful 4-line probe technique to measure additional parameters that determine cell power performance:
  - Anisotropic conductivity – measurement will be possible with N-line probe
  - Electronic conductivity changes when sample is wetted – previous work suggests this is a significant effect
  - Ionic conductivity – continued work is needed to increase measurement reliability
- Complete development of a predictive 3D microstructure model that is validated with
  - Experimental conductivity data
  - Experimental microstructure data
- Success in the above two areas will provide a suite of tools for optimizing fabrication processes of particle-based electrodes.

PROPOSED FUTURE WORK (MILESTONES)

- **June 2015:** Develop fabrication process and demonstrate viability of **micro-N-line probe**. *Justification:* The additional lines on the probe will allow us to measure anisotropic effects and increase measurement robustness. The model has already predicted significant anistropic effects.
- **Sept 2015:** (**Go/No-Go**) Discontinue dynamic particle-packing (DPP) model if it cannot be used to predict electrode configurations of real electrode materials as analyzed by FIB/SEM. *Justification:* We must prove or disprove the hypothesis that aggregates of spheres can be used to predict electrode structures of relevance to battery research. As an alternative pathway, we can use automated segmentation techniques from FIB/SEM images in further simulations of battery performance, though this gives us less predictive capability than our preferred method of using DPP to predict initial structures.
- **Dec 2015:** Demonstrate that the DPP model can accurately imitate the mechanical calendering process for a representative electrode film. *Justification:* This will greatly enhance the predictive capabilities of our model to capture manufacturing processes.
- **Mar 2016:** Develop a robust numerical routine for interpreting N-line conductivity measurements. *Justification:* While starting from the base code that we are currently using, this will incorporate greater statistical cross-checking and model estimation. This is necessary to successfully interpret N-line data.
- **June 2016:** (**Go/No-Go**) Continue work on N-line probe and inversion routine. *Justification:* While the initial four-line probe has been successful, whether or not the additional lines and inversion algorithms are successful will be verified.
- **Sept 2016:** Demonstrate correlations between DPP modeled conductivities and those determined by FIB/SEM and N-line probe. *Justification:* This step begins to link the microstructural modeling and measurements to provide a more complete picture of the battery electrode manufacturing process.
- In addition to these milestones and decision points in FY14/FY15, we will pursue new collaborations and leverage our current collaborations to assess additional electrode materials of interest to DOE, using our unique diagnostic tools.

SUMMARY

- Deliverables after second year of project
  - First-generation electronic probe completed and tested. Transfer of technology to A123 completed.
  - Initial modeling using DPP method shows predictive capability to capture important battery slurry and drying processes.

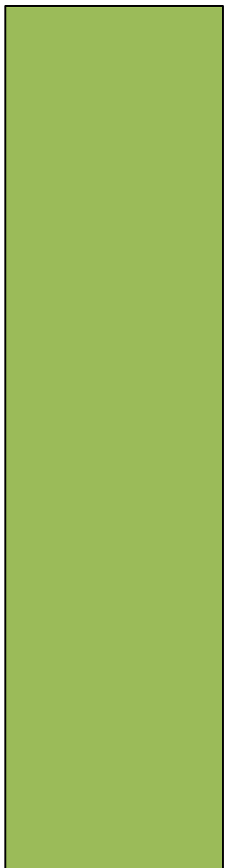
- How this will improve battery manufacturing
  - Commercial-grade electrodes have significant spatial differences in conductivity due to variability on the mm and smaller length scales.
  - Our suite of tools can quantify these differences and enable real-time quality control in roll-to-roll processing. It is anticipated that this will improve electrode utilization and cycle life.

Technical Back-up Slides

Comparative Microstructures

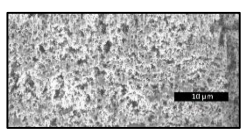
Carbon+Binder formulation

Liquid simulation



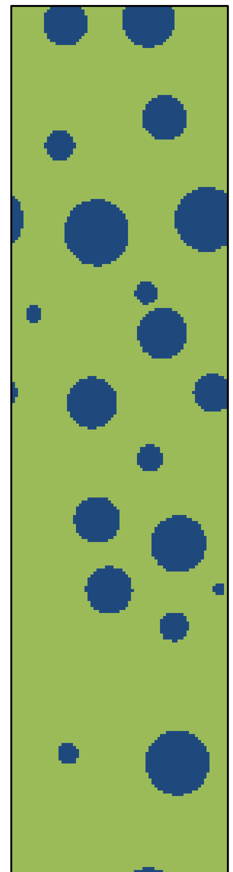
Dried film simulation

Experimental dried film



Active+Carbon+Binder formulation

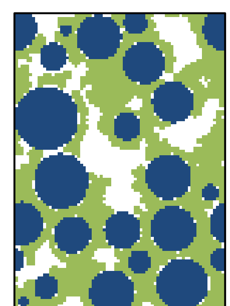
Liquid simulation



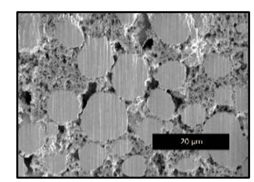
Volume Fractions of Active Film

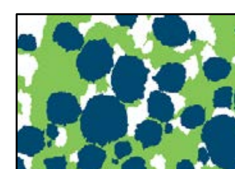
Domain	SEM/FIB	Sim
Active	0.443	0.402
CB+binder+nanopore	0.367	0.376
Macropore	0.190	0.222

Dried film simulation



Experimental dried film





SEM Images

Surfaces of *uncalendered* carbon film (left) and active film (right)

Exposed delaminated carbon film surface (left) and powder of Toda NCM 523 active material (right)